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Environmental Monitoring Branch
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**Study 304. Surface Water Monitoring for Pesticides in Agricultural Areas in Central Coast
and Southern California, 2017**

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1. INTRODUCTION

Surface water monitoring for pesticides in agricultural areas of California is one of the California Department of Pesticide Regulation's (CDPR's) key environmental monitoring projects. This project was initiated in 2008 with a long-term goal of collecting data to better assess potential impacts of pesticides from agricultural runoff on California aquatic environments. Project findings help guide CDPR in the development and implementation of regulatory and non-regulatory mitigation activities. CDPR focuses its monitoring on major agricultural areas in Central Coast and Southern California where pesticide uses were heavy and irrigation practices have high runoff potentials. The monitoring areas include major watershed drainages in Monterey, Santa Barbara, San Luis Obispo and Imperial Counties (Starmer 2010, 2013; Deng 2016a).

Preliminary monitoring results in the Central Coast and Southern California in recent years had been summarized in study reports (Deng 2014, 2015a&b, 2016b, 2017). Over 24 pesticides in 8 chemical groups were monitored each year. In 2016, malathion, dimethoate, methomyl, methoxyfenozide, bifenthrin, λ -cyhalothrin, permethrin and imidacloprid were the insecticides detected at high frequencies (20-89%) and the frequencies of their concentrations exceeding the lowest US EPA aquatic life benchmark values ranged from 9 to 46% (Deng 2017). Those insecticides are highly toxic to aquatic organisms. Many of them were commonly detected in single or multiple samples from the same watershed. Their frequent concurrent occurrences in a given watershed and frequent exceedances for their benchmarks indicate that the insecticide uses in the monitored watershed drainages could cause significant adverse impacts to non-targeted aquatic organisms and aquatic communities. Herbicides and fungicides that were frequently detected included atrazine, bensulide, oxyfluorfen, pendimethalin, azoxystrobin and pyraclostrobin (14-67%). However, the benchmark exceedances for herbicides and fungicides were at low frequencies.

Study 304 is a continuation of CDPR's agricultural monitoring efforts in Central Coast and Southern California. Monitoring sites were selected from those established in previous years

with no changes from 2016 (Deng 2016a). Priority lists of pesticides recommended for monitoring in each watershed were identified using CDPR's Prioritization Model (Luo et al. 2013, 2014, 2015). The watershed-based prioritization approach was applied to help refine the pesticide priority list for monitoring in 2017.

2. OBJECTIVE

The goal of the project is to assess short-term changes and long-term trends of pesticide contamination in agricultural runoff and the potential impacts of the runoff to aquatic environments. Results of the assessment will provide information to managers to make mitigation responses to potential environmental risks of pesticide contamination. Objectives of the project are as follows:

- 1) Prioritize pesticide monitoring candidates based on the current pesticide use report at watershed level;
- 2) Determine occurrences and measure chemical concentrations of high priority pesticides in runoff samples;
- 3) Analyze chemistry data to evaluate potential impacts on aquatic environments by comparing environmental concentrations with the US EPA aquatic life benchmarks;
- 4) Analyze spatial correlations between observed pesticide concentrations/detection frequencies and region-specific pesticide uses;
- 5) Assess multiple years of data to characterize patterns and trends in detection frequencies and benchmark exceedances.

3. PERSONNEL

The study will be conducted by staff from the Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Kean S. Goh Ph.D., Environmental Program Manager I. Key personnel are listed below:

Project Leader: Xin Deng, Ph.D.
Field Coordinator: Kevin Kelley
Review Scientist: Yuzhou Luo, Ph.D.
Statistician: Dan Wang, Ph.D.
Laboratory Liaison: Sue Peoples
Analytical Chemistry: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

Questions concerning this monitoring project should be directed to Xin Deng, Senior Environmental Scientist, at (916) 445-2506 or by email at xdeng@cdpr.ca.gov.

4. SELECTION OF PESTICIDES FOR MONITORING

The pesticides were prioritized following the procedures described in the Monitoring Prioritization Model (Luo et al. 2013, 2014, 2015). The watershed-based prioritization model uses 12-digit hydrologic units on the USGS Watershed Boundary Database (<http://viewer.nationalmap.gov/viewer/nhd.html?p=nhd>) to define the watershed boundary. It then aggregates the total use of each pesticide within the watershed and adjusts the total use by factoring in its dissipation as a function of travel time. The model was applied to generate ranked lists of pesticides for each watershed. Pesticides were then screened to produce final monitoring lists following the general criteria below:

- 1) Pesticides with final ranking scores ≥ 9 in a priority list for a watershed of interest will be monitored as pesticides with this ranking have higher uses (use scores ≥ 2) and toxicity (tox scores ≥ 3 , acute benchmark values ≤ 100 ppb), thus, have higher potential risks to aquatic communities.
- 2) Pesticides with final scores ≤ 8 and use scores ≥ 2 in a priority list will be considered for monitoring. The use criterion includes the top 30% pesticides with the highest use amounts among all the pesticides reported to PUR in 2012-2014 for a watershed of interest. Pesticides that are not in the priority lists or have use scores < 2 may be reported when they will be concurrently analyzed with other prioritized pesticides in an analytical group.
- 3) Historical monitoring data, current use trends, availability of analytical methods and budget constrains are additional factors to help decide a final list for monitoring.

5. STUDY PLAN

5.1. Imperial County

Ambient monitoring will be conducted in Imperial County twice a year in March and October. March and October will capture pesticide uses in winter and summer, respectively. Six sites that had been monitored within the watersheds of Alamo and New Rivers in 2016 were selected for monitoring in 2017 (Figure 1, Table 1).

The priority lists for monitoring in New River and Alamo River in March and October were generated using the average use data from January to March and from August to October in 2012-2014, respectively (Table 2 and 3). The chemical lists recommended by the model are similar to those in 2016. Paraquat dichloride that appeared on the priority list in the New River watershed in 2016 was not listed in 2017 due to its use reduction. Imidacloprid and bensulide will be included for monitoring despite their lower final scores on the priority list between

January and March because the two active ingredients have been frequently detected statewide in previous years. Chlorantraniliprole with a final score of 8 will be monitored in October due to its increasing uses in recent years (CDPR 2016).

5.2. Monterey County

Ambient monitoring will be conducted in Monterey County 6 times a year from April to September. Six sites that were monitored within the watersheds of Salinas River and Tembladero Slough in 2016 were selected for monitoring in 2017 (Figure 2, Table 1).

The priority lists for monitoring in each watershed were generated using the average pesticide use data from April to September in 2012-2014 (Table 4). The chemical lists recommended by the model are similar to those in 2016 with changes on rankings of a few chemicals due to changes of their use scores in recent years. Notably, the use amounts of chlorpyrifos and diazinon had significantly reduced so did their ranking scores on the priority list. Nevertheless, the monitoring results indicated over 10% detections for chlorpyrifos and 0-11% detections for diazinon in the last three years. We will keep monitoring the two chemicals in 2017.

Chlorantraniliprole and S-metolachlor with a final score of 8 will be monitored in the Salinas River watershed in 2017 due to their increasing uses in recent years. Paraquat dichloride herbicide and fenamidone fungicide are on the priority list in the Salinas River watershed but will not be monitored in 2017 due to either the low detection frequency statewide in previous years or unavailability of analytical methods (Table 4).

5.3. Santa Barbara and San Luis Obispo County

Ambient monitoring will be conducted in Santa Barbara and San Luis Obispo Counties 3 times a year in May, July and September. Four monitoring sites that had been monitored within the watersheds of Orcutt Creek and Oso Flaco Creek in 2016 were selected for monitoring in 2017 (Figure 3). Detailed information for the locations of current and previous sites is listed in Table 1.

The priority lists for monitoring in each watershed were generated using the average use data from April to September in 2012-14 (Table 5). The chemicals recommended by the model for monitoring in the Orcutt Creek watershed are similar to those in 2016. Chlorpyrifos dropped out of the lists for both watersheds but will be kept on the monitoring list in 2017 as part of the multi-analyte screen. Bifenthrin, methomyl and cyprodinil that were not on the monitoring list in Orcutt Creek in 2016 appeared on the 2017 list and will be monitored. Fenhexamid fungicide is on the priority list for the Oso Flaco Creek watershed (Table 5) but will not be monitored because the analytical method is not currently available.

6. SAMPLING METHOD

6.1. Water Sampling and Sample Transport

Water samples will be collected as grab samples directly into 1-liter amber glass bottles sealed with Teflon-lined lids. Samples will be transported and stored on wet ice or refrigerated at 4°C until analyzed. CDPR staff will transport samples following the procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999). A chain-of-custody record will be completed and accompany each sample.

6.2. Field Measurements

Dissolved oxygen, pH, specific conductivity, turbidity and water temperature will be measured *in situ* during each sampling event with an YSI EXO1 multi-parameter water quality Sonde (Doo and He 2008).

7. LABORATORY ANALYSES

7.1. Chemical Analysis

Chemical analyses will be performed by the Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento, CA. A total of 30 pesticides will be analyzed in water samples collected from 3 counties in 2017. Pesticides selected for each county for the monthly sampling event are listed in Table 6. Many of the pesticides in the screening groups will be selected from a single liquid chromatograph multi-analyte screen (LC-screen). Method detection limits and reporting limits for each chemical are presented in Table 7. Quality control will be conducted in accordance with the Standard Operating Procedure QAQC001.00 (Segawa 1995). Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Segawa 1995). Laboratory blanks and matrix spikes will be included in each extraction set.

7.2. Organic Carbon and Suspended Solid Analysis

Total organic carbon (TOC) and dissolved organic carbon (DOC) in water samples will be analyzed by CDPR staff using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan) (Ensminger 2013a). Water samples will also be analyzed for suspended sediment (Ensminger 2013b). Lab blanks and calibration standards will be run before every sample set to ensure the quality of the data.

7.3. Toxicity Analysis

Toxicity analyses will be conducted for water samples collected from a subset of sampling sites by the Aquatic Health Program or the Granite Bay Marine Pollution Laboratory at the University

of California, Davis. Grab water samples will be tested for mortality using *Hyaella azteca*, *Chironomus dilutus* or *Ceriodaphnia dubia* as surrogate species.

8. DATA ANALYSIS

All data generated by this project will be entered in a Microsoft Office Access database that holds field information, field measurements, and laboratory analytical data. All ambient monitoring analytical data will also be uploaded into the CDPR Surface Water Database (SURF) (<http://cdpr.ca.gov/docs/emon/surfwtr/surfddata.htm>).

Resulting data will be analyzed and reported as appropriate, potentially including the following: Comparison of pesticide concentrations to aquatic toxicity benchmarks, water quality limits and other toxicity data (CCVRWQCB 2012, US EPA 2015); spatial analysis of data in order to identify correlations between observed pesticide concentrations and region-specific pesticide uses and geographical features; assessment of multiple years of data to characterize patterns and trends in detection frequencies; assessment of results to determine potential additional monitoring in regions with similar pesticide use patterns.

9. TIMETABLE

Field Sampling:	March 2017 — October 2017
Chemical Analysis:	March 2017 — December 2017
Draft Report:	March 2017
Data Entry into SURF:	April 2017

10. SAMPLING EVENTS AND BUDGET

The monthly sampling schedule for each county and the estimated total cost for chemical analyses were provided in Table 8.

11. REFERENCES

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Table 1. Sampling Site Information for Study 304 in 2017

Site ID	Site Location	County	Watershed	Latitude	Longitude	Site Type
Imp_NewRiv27	New River at HWY S27/Keystone Road	Imperial	New River	32.9136	-115.60646	Main Stream
Imp_Lack	New River at Lack Road			33.0999	-155.64876	Main Stream
Imp_Rice3	Rice Drain III at Weinert Road			32.8691	-115.651	Ag Drain
Imp_Rutherford	Alamo River at Rutherford Rd (upstream of Imperial State Wildlife Area)		Alamo River	33.0447	-115.48829	Main Stream
Imp_Garst	Alamo River at Garst Road			33.199	-115.59696	Main stream
Imp_Holtville	Holtville Main Drain at HWY115			32.9309	-115.40611	Ag Drain
Sal_Quail	Quail Creek at HWY 101, btwn Spence and Potter Roads	Monterey	Salinas River	36.6092	-121.56269	Tributary
Sal_Chualar	Chualar Creek at Chualar River Rd., ca. 1.2 mi. from HWY 101			36.5584	-121.52964	Tributary
Sal_Davis	Salinas River at Davis Road			36.647	-121.70219	Main Stream
Sal_Hartnell	Alisal Creek at Hartnell Rd		Tembladero Slough	36.6435	-121.57836	Tributary
Sal_SanJon	Rec Ditch at San Jon Road			36.7049	-121.70506	Tributary
Sal_Haro	Tembladero Slough at Haro Street			36.7596	-121.75433	Main Stream
SM_OFC	Oso Flaco Creek @ OFL Road	San Luis Obispo	Oso Flaco Creek	35.0164	-120.58755	Tributary
SM_Solomon	Solomon Creek @ HWY 1	Santa Barbara	Orcutt Creek	34.9414	-120.5742	Main Stream
SM_Orcutt	Orcutt Creek @ Main Street			34.9576	-120.63244	Main Stream
SM_Bradley	Bradley Channel @ River Oaks		Bradley Channel	34.9742	-120.4245	Ag drain

Table 2. Pesticide Prioritization for Surface Water Monitoring in Alamo River and New River in Imperial County. Ranking of Pesticides Based on Average Use Data from January to March in 2012-2014

Alamo River, Drainage Area = 1264 km²				
Chemical	Use score	Tox score	Final score	Monitoring inclusion
Chlorpyrifos	5	6	30	Yes
Atrazine	3	8	24	Yes
Pendimethalin	5	4	20	Yes
Trifluralin	5	4	20	Yes
Malathion	4	5	20	Yes
Permethrin	3	6	18	Yes
λ-cyhalothrin	2	7	14	Yes
Dimethoate	4	3	12	Yes
Methomyl	3	4	12	Yes
Cypermethrin	2	5	10	Yes
Oxyfluorfen	2	5	10	Yes
Bensulide	4	2	8	Yes
Imidacloprid	2	3	6	Yes
Indoxacarb	2	3	6	Yes
New River, Drainage Area = 1729 km²				
Chemical	Use score	Tox score	Final score	Monitoring inclusion
Chlorpyrifos	4	6	24	Yes
Atrazine	3	8	24	Yes
Pendimethalin	5	4	20	Yes
Trifluralin	5	4	20	Yes
Malathion	4	5	20	Yes
Permethrin	3	6	18	Yes
λ-cyhalothrin	2	7	14	Yes
Dimethoate	4	3	12	Yes
Methomyl	3	4	12	Yes
Cyfluthrin	2	6	12	Yes
Cypermethrin	2	5	10	Yes
Oxyfluorfen	2	5	10	Yes
Bensulide	3	2	6	Yes
Indoxacarb	2	3	6	Yes

Table 3. Pesticide Prioritization for Surface Water Monitoring Alamo River and New River in Imperial County. Ranking of Pesticides Based on Average Use Data from August to October in 2012-2014

Alamo River, Drainage Area = 1264 km²				
Pesticide	Use score	Tox score	Final score	Monitoring inclusion
Chlorpyrifos	4	6	24	Yes
Atrazine	2	8	16	Yes
Pendimethalin	3	4	12	Yes
Trifluralin	3	4	12	Yes
Permethrin	2	6	12	Yes
Esfenvalerate	2	6	12	Yes
Bensulide	5	2	10	Yes
Cypermethrin	2	5	10	Yes
Malathion	2	5	10	Yes
Oxyfluorfen	2	5	10	Yes
Imidacloprid	3	3	9	Yes
Methoxyfenozide	3	3	9	Yes
Methomyl	2	4	8	Yes
Chlorantraniliprole	2	4	8	Yes
New River, Drainage Area = 1729 km²				
Pesticide	Use score	Tox score	Final score	Monitoring inclusion
Chlorpyrifos	4	6	24	Yes
Pendimethalin	3	4	12	Yes
Trifluralin	3	4	12	Yes
Permethrin	2	6	12	Yes
Bensulide	5	2	10	Yes
Malathion	2	5	10	Yes
Paraquat dichloride	2	5	10	No ¹
Cypermethrin	2	5	10	Yes
Imidacloprid	3	3	9	Yes
Methomyl	2	4	8	Yes
Chlorantraniliprole	2	4	8	Yes

Notes for exclusion:

- 1) Low detection frequencies statewide (less than 1 % detection in 1828 samples; SURF database, 2016) from monitoring results in previous years.

Table 4. Pesticide Prioritization for Surface Water Monitoring in Salinas River and Tembladero Slough in Monterey County. Ranking of Pesticides Based on Average Use Data from April to September in 2012-2014

Salinas River, Drainage Area = 11082 km²				
Pesticide	Use score	Tox score	Final score	Monitoring inclusion
Permethrin	3	6	18	Yes
Methomyl	4	4	16	Yes
Malathion	3	5	15	Yes
Paraquat dichloride	3	5	15	No ¹
λ-cyhalothrin	2	7	14	Yes
Chlorpyrifos	2	6	12	Yes
Bensulide	5	2	10	Yes
Oxyfluorfen	2	5	10	Yes
Imidacloprid	3	3	9	Yes
Cyprodinil	3	3	9	Yes
Fenamidone	3	3	9	No ²
Pyraclostrobin	2	4	8	Yes
Prometryn	2	4	8	Yes
S-metolachlor	2	4	8	Yes
Chlorantraniliprole	2	4	8	Yes
Diazinon	1	5	5	Yes
Tembladero Slough, Drainage Area = 291 km²				
Pesticide	Use score	Tox score	Final score	Monitoring inclusion
Malathion	4	5	20	Yes
Permethrin	3	6	18	Yes
Methomyl	3	4	12	Yes
Bifenthrin	2	6	12	Yes
Cyprodinil	3	3	9	Yes
Diazinon	1	5	5	Yes

Notes for exclusion:

- 1) Low detection frequencies statewide (less than 1 % detection in 1828 samples; SURF database, 2016) from monitoring results in previous years.
- 2) Analytical method not currently available.

Table 5. Pesticide Prioritization for Surface Water Monitoring in Orcutt Creek and Oso Flaco Creek in Santa Barbara and San Luis Obispo Counties. Ranking of Pesticides Based on Average Use Data from April to September in 2012-2014

Orcutt Creek, Drainage Area = 301 km²				
Pesticide	Use score	Tox score	Final score	Monitoring inclusion
Malathion	5	5	25	Yes
Oxyfluorfen	3	5	15	Yes
Imidacloprid	4	3	12	Yes
Prometryn	3	4	12	Yes
Pyraclostrobin	3	4	12	Yes
Permethrin	2	6	12	Yes
Bifenthrin	2	6	12	Yes
Fenpropathrin	2	5	10	Yes
Cyprodinil	3	3	9	Yes
Bensulide	4	2	8	Yes
Trifluralin	2	4	8	Yes
Methomyl	2	4	8	Yes
Oso Flaco Creek, Drainage Area = 51 km²				
Pesticide	Use score	Tox score	Final score	Monitoring inclusion
Malathion	5	5	25	Yes
Oxyfluorfen	3	5	15	Yes
Bifenthrin	2	6	12	Yes
Permethrin	2	6	12	Yes
Fenpropathrin	2	5	10	Yes
Imidacloprid	3	3	9	Yes
Fenhexamid	4	2	8	No ¹
Pyraclostrobin	2	4	8	Yes
Trifluralin	2	4	8	Yes

Notes for exclusion:

- 1) Analytical method not currently available.

Table 6. Pesticides Monitored by County or Counties in Each Month in 2017

Analytic Screen	Pesticide	March	April- September	May, July, September	October
		Imperial	Monterey	Santa Barbara, San Luis Obispo	Imperial
Liquid chromatograph multi-analyte screen (LC)	Atrazine	x			x
	Azoxystrobin		x	x	
	Bensulide	x	x	x	x
	Chlorantraniliprole	x	x	x	x
	Chlorpyrifos	x	x	x	x
	Cyprodinil		x	x	
	Diazinon		x		
	Dimethoate	x	x	x	x
	Imidacloprid	x	x	x	x
	Indoxacarb	x			
	Malathion	x	x	x	x
	Methomyl	x	x	x	x
	Methoxyfenozide	x	x	x	x
	Prometryn		x	x	
	Pyraclostrobin		x	x	
S-Metolachlor		x			
Dinitroanilines and Oxyfluorfen (DN/OX)	Benfluralin	x	x	x	x
	Ethalfuralin	x	x	x	x
	Oryzalin	x	x	x	x
	Oxyfluorfen	x	x	x	x
	Pendimethalin	x	x	x	x
	Prodiamine	x	x	x	x
	Trifluralin	x	x	x	x
Pyrethroids (PY)	Bifenthrin	x	x	x	x
	λ -cyhalothrin	x	x	x	x
	Permethrin (cis)	x	x	x	x
	Permethrin (trans)	x	x	x	x
	Cyfluthrin	x	x	x	x
	Cypermethrin	x	x	x	x
	Fenpropathrin	x	x	x	x
	Fenvalerate Esfenvalerate	x	x	x	x

Table 7. Reporting Limit and Method Detection Limit for Pesticides Monitored in 2017

Analytic Screen	Pesticide	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Liquid chromatograph multi-analyte screen (LC)	Atrazine	0.004	0.02
	Azoxystrobin	0.004	0.02
	Bensulide	0.004	0.02
	Chlorantraniliprole	0.004	0.02
	Chlorpyrifos	0.004	0.02
	Cyprodinil	0.004	0.02
	Diazinon	0.004	0.02
	Dimethoate	0.004	0.02
	Imidacloprid	0.004	0.02
	Indoxacarb	0.004	0.02
	Malathion	0.004	0.02
	Methomyl	0.004	0.02
	Methoxyfenozide	0.004	0.02
	Prometryn	0.004	0.02
	Pyraclostrobin	0.004	0.02
	S-Metolachlor	0.004	0.02
Dinitroanilines and Oxyfluorfen (DN/OX)	Benfluralin	0.015	0.05
	Ethalfluralin	0.017	0.05
	Oryzalin	0.021	0.05
	Oxyfluorfen	0.023	0.05
	Pendimethalin	0.019	0.05
	Prodiamine	0.02	0.05
Pyrethroids (PY)	Trifluralin	0.015	0.05
	Bifenthrin	0.00091	0.001
	Lambda-cyhalothrin	0.00174	0.002
	Permethrin (cis)	0.00105	0.002
	Permethrin (trans)	0.00105	0.005
	Cyfluthrin	0.00146	0.002
	Cypermethrin	0.00154	0.005
	Fenpropathrin	0.00132	0.005
Fenvalerate/esfenvalerate	0.00166	0.005	

Table 8. Number of Samples Collected for Pesticide Analyses for the County or Counties and Associated Budget in March – October, 2017

Analyte Group*	March	April	May	June	July	August	September	October	Total Number of Samples	QC Samples	Cost Per Sample	Total Cost Per Analyte Group
	Imperial	Monterey	Monterey SB and SLO****	Monterey	Monterey SB and SLO	Monterey	Monterey SB and SLO	Imperial				
LC-Screen	4**	6	10	6	10	6	10	4	56	6	1,700	105,400
DN/OX	4	6	10	6	10	6	10	4	56	6	840	52,080
MA-A	4	6	10	6	10	6	10	4	56	6	510	31,620
PY	6	6	10	6	10	6	10	6	60	6	600	39,600
Grand Total	14	24	40	24	40	24	40	18	228	24	3,650	228,700

* LC-screen = Liquid chromatograph multi-analyte screen; DN/OX = Dinitroaniline & Oxyfluorfen; MA-A = Malathion acidified; PY = Pyrethroid

** The number represents total number of samples collected for each analyte or analyte group. One grab sample for each analyte or analyte group will be collected from one site

***SB = Santa Barbara; SLO = San Luis Obispo



Figure 1. Monitoring Sites in Alamo River and New River in Imperial County

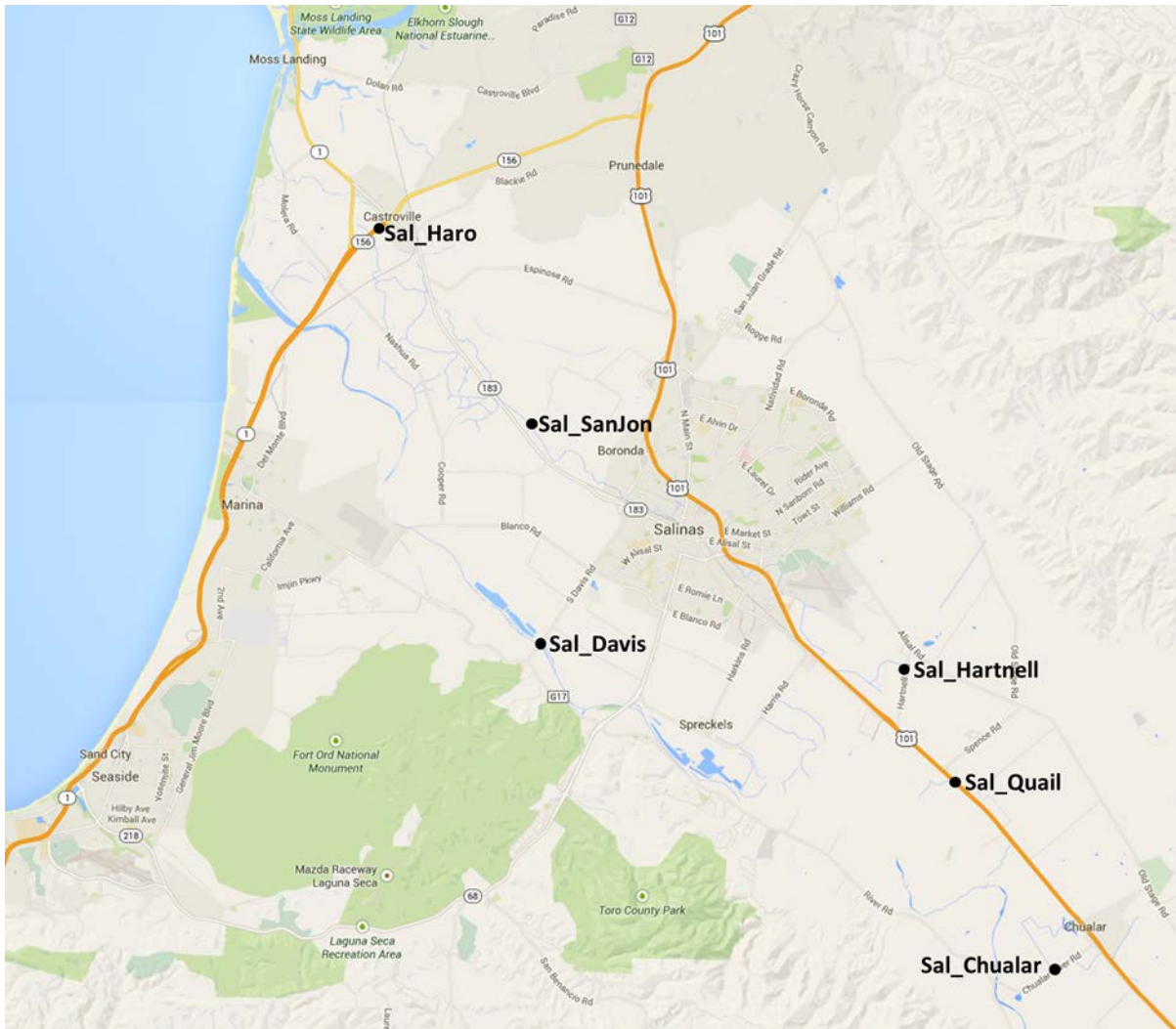


Figure 2. Monitoring Sites in Salinas River and Tembladero Slough in Monterey County

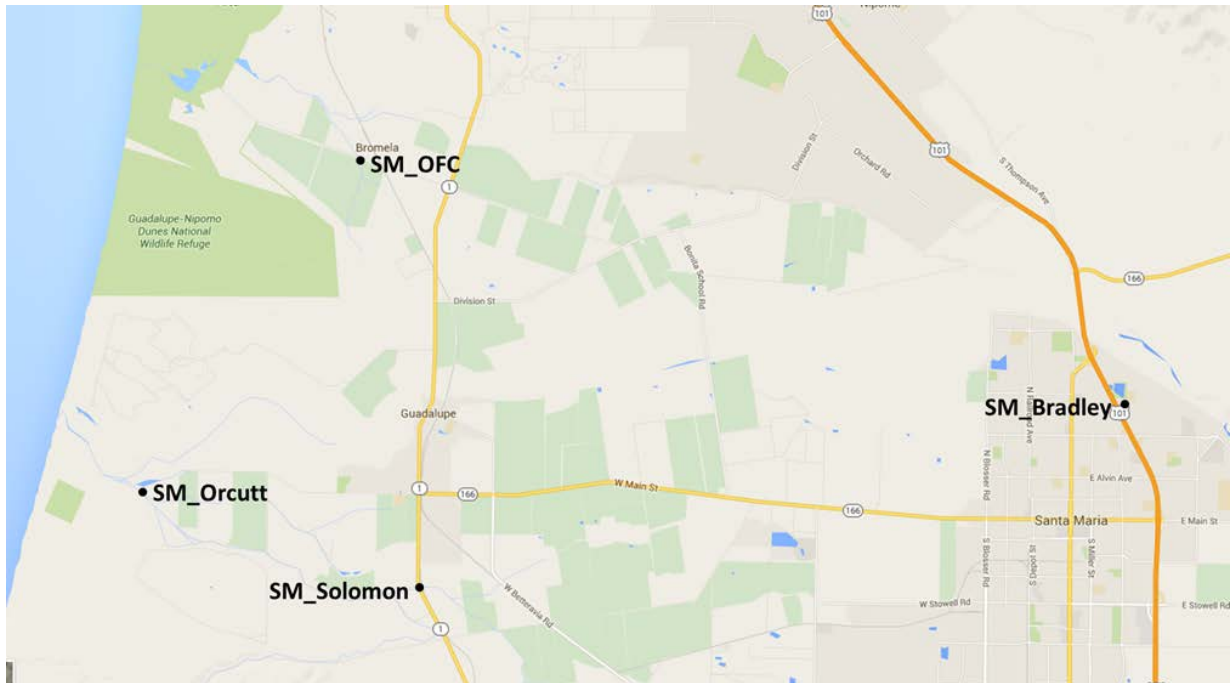


Figure 3. Monitoring Sites in Orcutt Creek and Oso Flaco Creek in Santa Barbara and San Luis Obispo Counties